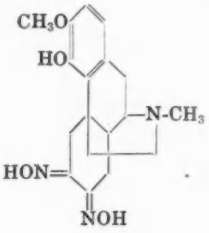
SINOMENIN UND DISINOMENIN XXXII.[1] ÜBER DEN HOFMANNSCHEN ABBAU VON 1-BROM SINOMENINON-DIOXIM UND DIE BROMIERUNG VON DEN SINOMENININON-FURAZAN-DERIVATEN.

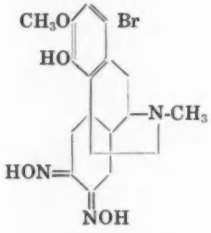
Von **Kakuji GOTO** und **Shingo MITSUI.**

Eingegangen am 21. Mai 1932. Ausgegeben am 28. Juli 1932.

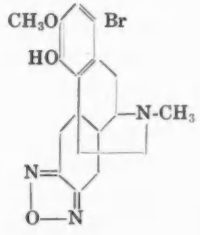
In der XXVII Mitteilung[2] dieser Untersuchung haben wir über den Hofmannschen Abbau von Sinomeninon-dioxim[3] [I] berichtet. Wir wollen jetzt Versuche angestellt um zu sehen ob 1-Brom-sinomeninon-dioxim [II] auch zu demselben Abbau zugänglich ist.



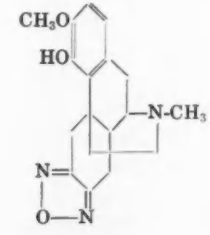
[I]



[II]



[III]



[IV]

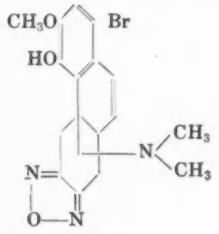
(1) XXIX Mitteilung, *Ann.*, **489** (1931), 86; XXX Mitteilung, *Ann.*, **494** (1932), 1; XXXI Mitteilung, *Ann.*, **495** (1932), 122.

(2) Diese Bulletin, **6** (1931), 197.

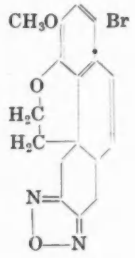
(3) Der dort angegebene Name Sinomeninhydrat-dioxim darf mit dieser neuen Bezeichnung ersetzt werden, da bei der weiteren Untersuchung sich ergeben hat dass das Sinomeninhydrat nichts anders als das Sinomeninon-methylalkoholat ist.

Wenn man 1-Brom-sinomeninon-dioxim mit 16.5 proc. Kalilauge einstundenlang kocht, so krystallisiert sich 1-Brom-sinomeninon-furazan [III] in schönen Prismen noch in der heissen Flüssigkeit. Die Tatsache dass in dieser Substanz wirklich ein Furazankern geschlossen ist, wird dadurch bewiesen dass Sinomeninon-furazan [IV] durch Bromierung mit ein Mol. Brom dieselbe Substanz gibt.

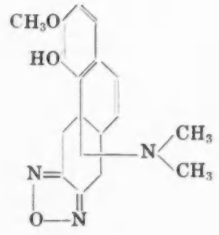
Das Jodmethylat von 1-Brom-sinomeninon-dioxim gibt beim Kochen mit 16.5 proc. Kalilauge des-N-Methyl-1-brom-sinomeninon-furazan [V]. Das Jodmethylat der letzteren Substanz ist nicht krystallisierend, aber wird es wieder durch Kochen mit 16.5 proc. Kalilauge ins 1-Brom-dehydro-*l*-thebenon-7-keton-furazan [VI] abgebaut.



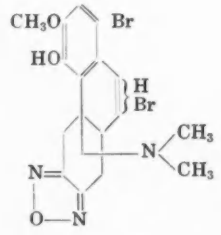
[V]



[VI]



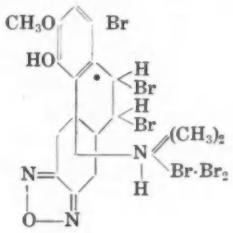
[VII]



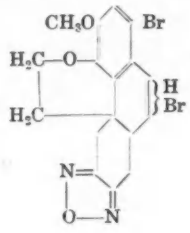
[VIII]

Wie oben angeführt, gibt Sinomeninon-furazan [IV] bei der Bromierung 1-Brom-sinomeninon-furazan [III]. Aber die Bromierung von des-N-Methyl-sinomeninon-furazan [VII] gibt des-N-Methyl-1-brom-sinomeninon-furazan [V] in einer sehr schlechten Ausbeute. Hier scheint die Bromierung an der Doppelbindung C_9-C_{10} nebeneinander sich vorzugehen. Durch Bromierung mit 2 Mol. Brom gibt dieselbe Substanz des-N-Methyl-dibrom-sinomeninon-furazan [VIII]. Von den zwei Bromatomen, muss der eine an C_1 sich befinden, sowohl aus der

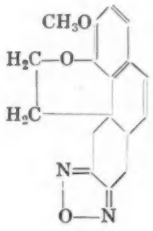
Analogie mit Sinomenin auch aus der starken Abnahme von Diazoreaktion. Für den anderen Bromatom müssen wir die Stellung C_9 oder C_{10} zuerteilen aus den Gründen, zu den wir später zurückkehren wollen.



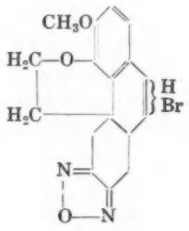
[IX]



[X]



[XI]

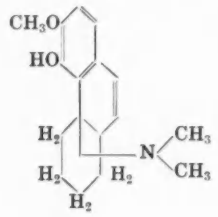


[XII]

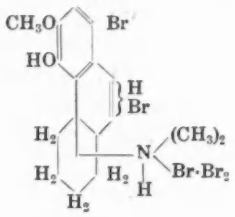
Bromierung von der des-N-Methyl-substanz [VII] mit drei Mol. Brom gestaltet sich etwas anders und man gewinnt dabei ein schön krystallisierendes Perbromid [IX]. Dieser Perbromid ist beständig gegen Eisessig, aber wird er sehr leicht durch Aceton zersetzt und dabei nimmt man die Entwickelung eines zum Tränen reizenden Gases (Monobromaceton?) wahr. Dieser Perbromid enthält sechs Atome Brom und wird durch Aceton und nachfolgende Behandelung mit Ammoniak in die Dibromsubstanz [VIII] umwandelt, aber die Rückumwandlung, d.h. die Darstellung dieses Perbromides durch die Anlagerung von 1 Mol. Brom an die Substanz [VIII] ist unmöglich. Daraus folgt dass in diesem Perbromid ein Bromatom an C_1 ersetzt und zwei Bromatome sich an der Doppelbindung C_9-C_{10} addiert haben müssen. Die äusserst grosse Krystallisationsfähigkeit dieses Perbromid scheint das Fortreissen eines Bromwasserstoffs aus C_9-C_{10} zu verhindern. Bromierung an C_5 oder C_8 ist auch hier aus den später zu erläuternden Gründen ausgechlossen.

Hofmannscher Abbau von dieser des-N-Methyl-dibrom-substanz [VIII] gibt einen 1,9?-Dibrom-dehydro-thebenon-7-keton-furazan [X],

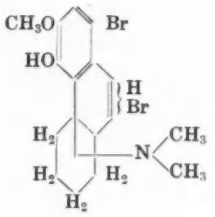
welches seinerseits auch durch Bromierung von Dehydro-thebenon-7-keto-furazan [XI] mit 2 Mol. Brom sich entstehen lässt. Aber bei der Bromierung von der letzteren Substanz [XI] mit 1 Mol. Brom tritt der Brom-atom zuerst in C_9 oder C_{10} ein, weil die resultierende Substanz [XII] ganz verschieden von dem 1-Brom-dehydro-thebenon-7-keto-furazan [VI] ist. Durch Bromierung von diesen



[XIII]



[XIV]



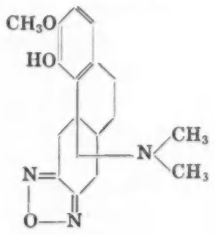
[XV]

zwei verschiedene Monobrom-derivate wieder mit 1 Mol. Brom wird ein und dasselbe Dibrom-dehydro-thebenon-7-keto-furazan [X] gebildet.

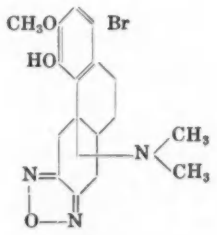
In der obigen Auseinandersetzungen, ist es schwer zu bestimmen ob der zweite Bromatom an C_9 oder C_{10} sich befindet. Das Verhältnis scheint ganz ähnlich mit dem Fall von Monobrom-phenanthren zu sein. Die Tatsache dass der zweite Bromatom sich nicht in dem hydrierten Kern des Phenanthrens befinden kann, wurde dadurch bewiesen dass das Dibrom-dehydro-*l*-thebenon-7-keto-furazan gegen Kochen mit methyl-alkoholischen Kali oder mit Silberacetat in Eisessig ganz beständig ist. Es ist klar dass die Bromierung an C_9 oder C_{10} dadurch zustande kommt, indem zuerst 1 Mol. Brom sich an der Doppelbindung C_9-C_{10} addiert und dann ein Molekül Bromwasserstoff abgespaltet wird. Nur scheint in dem Perbromid von des-N-Methyl-1-brom-sinomeninon-furazan-dibromid [9, 10] diese Abspaltung von Bromwasserstoff verhindert werden zu sein, so lange er als solches in Krystallform sich befindet. Aber welcher von diesen zwei Brom-atomen abgespalt wird und welcher zurückbleibt, können wir zurzeit nicht bestimmen. Nur aus der Analogie mit Zimtsäuredibromid, welches bei der Behandlung mit Alkali ω-Brom-styrol gibt, sind wir geneigt anzunehmen dass der Bromatom an C_{10} fortgerissen werden und der an C_9 zurückbleiben muss.

Um diesen Punkt und sowohl auch die Annahme genauer bestättigen dass die Furazan-gruppe, im Gegensatz zu der freien Ketongruppe, keine merkliche dirigierende Wirkung auf dem Bromatom ausübt, haben wir in der zweierlei Richtungen die Versuche angestellt. Zuerst haben wir

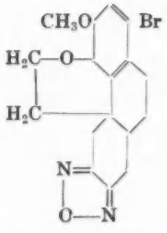
des-N-Methyl-demethoxy-desoxo-dihydro-sinomenin [XIII] mit 3 Mol. Brom bromiert. Dann haben wir das Perbromid von Dibrom-demethoxy-desoxo-dihydro-sinomenin [XIV] bekommen, welches merklicherweise nur fünf Atome Brom enthält. Die daraus befreite Base enthält auch nur zwei Brom-atome. So ist es klar dass das Perbromid von dieser Substanz [XIV] als solches schon ein Mol. Bromwasserstoff aus C_9-C_{10} abgespaltet haben muss. Dieser merkwürdige Unterschied zwischen den beiden Perbromiden [IX] und [XIV] muss wahrscheinlich seine Ursache in der Furazangruppe in [IX] haben. Zweitens haben wir Dihydro-des-N-methyl-sinomeninon-furazan [XVI] mit 1, 2, 3 Mol. Brom bromiert und nur ein einziges Produkt als Krystalle bekommen d.h. Dihydro-des-N-methyl-1-brom-sinomeninon-furazan [XVII]. Nur vermindert die Ausbeute nach der Menge des angewandten Broms. Daraus folgt dass das Brom hier einiger massen oxydative Wirkung ausüben kann, aber als ein einheitliches Produkt nur das 1-bromierte Substanz gibt. Die Stellung-1 wurde aus der Analogie mit 1-Brom-sinomenin und aus der sehr verminderten Diazoreaktion angenommen. Das Jodmethylat von diesem Dihydro-des-N-Methyl-1-brom-sinomeninon-furazan [XVII] schliesst sehr leicht seinen Oxydring und gibt 1-Brom-*l*-thebenon-7-keto-furazan [XVIII].



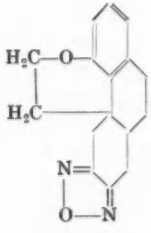
[XVI]



[XVII]



[XVIII]



[XIX]

Die letzte Substanz wird auch durch Bromierung von *l*-Thebenon-7-keto-furazan [XIX] mit 1 Mol. Brom sehr leicht dargestellt.

Zusammenfassung.

Aus diesen Versehen ergeben sich

1. 1-Brom-sinomeninon-dioxim bildet ein Furazan ebenso leicht wie Sinomeninon-dioxim.
2. Ein schwerer Atom wie Brom in der Para-stellung zu der freien Phenolgruppe verhindert nicht den Thebenon-ringschluss.
3. In Thebenon kann die Para-stellung zu der Oxido-O ebenso leicht bromiert werden, wie diejenige zur freien Phenolgruppe.(1)
4. In Dehydro-thebenon (= 7-keto-furazan), indessen, wird zuerst die Doppelbindung bromiert und dann die Para-stellung zur Oxido-O.
5. Perbromide von zwei des-N-Methyl-basen wurden in wohl krystallisierender Form isoliert und beschrieben.

Beschreibung der Versuche.

1. 1-Brom-sinomeninon-furazan (III). *Durch Furazan-ringschluss.* 1.0 gr. Brom-sinomeninon-dioxim (II) wird mit 10 ccm. 16.5 proc. Kalilauge einstundenlang gelinde gekocht. Schon nach fünf Minuten scheidet das Furazan in sandigen Krystallen aus. Ausbeute etwa 50 Proc. Zum Umkrystallisieren wird es in sehr verdünnter Salzsäure gelöst, dann mit konzentrierter Natronlauge kochend ausgefällt. Farblose dicke Prismen von Zers. 262°C.

Durch Bromierung. 0.5 gr. Sinomeninon-furazan (IV) wird in 10 ccm. Eisessig mit 1.5 gr. Brom (in 5 ccm. Eisessig gelöst) bei 16°C. bromiert. Nach eintägigem Stehenlassen bei der Zimmertemperatur wird die Reaktionsprodukt auf 70° ~ 90°C. bis zum vollständigen Auflösen des ausgeschiedenen Perbromids erwärmt. Man entfernt den Überschuss von Brom mit Natriumsulfit. Die daraus befreite Base wird mit Chloroform extrahiert und in der oben beschriebenen Weise gereinigt.

Mischschmelzp. zeigt keine Depression.

Subst. = 4.186 mg.; AgBr = 1.894 mg. Gef.: Br = 19.26%.
Ber. für $C_{18}H_{20}O_3N_3Br$ (406): Br = 19.68%.

2. des-N-Methyl-1-brom-sinomeninon-furazan (V). *Aus 1-Brom-sinomeninon-dioxim-jodmethylat.* Das Jodmethylat wird in üblicher Weise dargestellt. Zers. 254°C. (sintern 220°C.).

(1) Hierzu vergleiche auch C. Schöpf u. T. Pfeifer, *Ann.* **483** (1930), 167.

Subst. = 0.0688: AgJ = 0.0284 gr. Gef.: J = 22.31%.
Ber. für $C_{18}H_{22}O_4N_3Br\,JCH_3$ (566): J = 22.44%.

Dieses Jodmethylat wird in ganz analoger Weise wie bei der Furazan-Bildung mit 16.5 Proc. Kalilauge zur des-N-Methyl-Base abgebaut. Mit Wasser und Methanol gut nachgewaschen. Ausbeute etwa 65 Proc. d. Th. Prismen vom Zers. 225°C. Halochromie mit konz. Schwefelsäure orangerot.

Durch Bromierung. Zum 0.5 gr. des-N-Methyl-sinomeninon-furazan (VII), gelöst in 10 ccm. Eisessig, setzt man 0.24 gr. Brom (1 Mol. mit 2.4 ccm. Eisessig verdünnt) bei 15°C. tröpfenweise zu. Nach üblicher Behandlung erhält man Krystallen in einer sehr schlechten Ausbeute, die sich aus dem Mischschmelzp. nichts anders als (V) erweist.

Anal.: Subst. = 6.759: CO_2 = 13.320; H_2O = 3.346 mg.
Subst. = 9.196; AgBr = 2.839 mg. Subst. = 4.534 mg.; N_2 = 0.393 ccm., 18.5°C., 755 mm.
Gef.: C = 53.74; H = 5.50; Br = 19.52; N = 9.88%.
Ber. für $C_{19}H_{22}O_3N_3Br$ (420): C = 54.03; H = 5.24; Br = 19.03; N = 10.00%.

3. des-N-Methyl-1,9?-dibrom-sinomeninon-furazan (VIII). *Durch Bromierung.* 2.0 gr. des-N-Methyl-sinomeninon-furazan VII werden in 30 ccm. Eisessig gelöst, mit 1.8 gr. Brom (etwa 2 Mol. gelöst in 18 ccm. Eisessig) bei 15°C. bromiert und übernacht stehen gelassen. Nach dem kurzen Erwärmen (10 Minuten) auf 100°C. wird der Eisessig unter vermindertem Druck abdestilliert, der ölige Rückstand in 15 ccm. Aceton aufgenommen, mit verdünntem Ammoniak (1:3) tröpfenweise versetzt und kurz erwärmt. Dabei krystallisert das dibromierte Produkt in einer etwa theoretischen Ausbeute.

Aus Methanol gereinigt, stellt es schöne Prismen vom Zers. 212°C. (sintern 194°C.) dar. In konz. Schwefelsäure setzt, zeigt es eine orangegelbe→gelblichbraune→braune Halochromie.

Durch Abbau des Perbromids. Die Abspaltung der perbromidartig gebundenen Brom-atomen erfolgt sich sehr leicht sowohl durch Aceton als auch durch schwefelige Säure.

(1) 2.0 gr. Perbromid (IX) werden mit 10 ccm. Aceton entweder mehrere Tage bei der Zimmertemperatur oder halbstundenlang auf 100°C. digeriert. Dabei nimmt man eine heftige Entwickelung eines lachrymatorischen Gases (Monobromaceton?) wahr. Ausbeute: 0.7 gr.

(2) 0.5 gr. Perbromid (IX) wird in 10 ccm. Wasser suspendiert, und in dieser Suspension wird ein langsamer Strom von SO_2 10 Minutenlang eingeleitet. Da das dabei entstehende Bromhydrat von (VIII) keine Neigung zur Krystallisation zeigt, wird es in Methanol durch Ammoniak befreit und als die freie Base (VIII) erkannt. Ausbeute gut.

Anal.: Subst. = 4.117; CO_2 = 6.923; H_2O = 1.573 mg.
Subst. = 4.421; AgBr = 3.367 mg. Subst. = 3.595 mg.; N_2 = 0.261 ccm. 17°C., 767 mm.
Gef.: C = 45.86; H = 4.25; Br = 32.41; N = 8.47%.
Ber. für $C_{19}H_{21}O_3N_3Br_2$ (490): C = 45.69; H = 4.21; Br = 32.03; N = 8.42%.

4. Perbromid von des-N-Methyl-1-brom-sinomeninon-furazan-dibromid (9, 10) (IX). Man löst 1.0 gr. des-N-Methyl-sinomeninon-furazan (VII) in 20 ccm. Eisessig und tröpft 1.5 gr. Brom (3 Mol.) in 15 ccm. Eisessig bei 15°C. etwas schnell und mit konstantem Turbinieren zu. Dann wird die Reaktionsprodukt auf 40°C. halbstundenlang erwärmt, zuletzt kurz auf 90°C. Dabei scheidet das Perbromid in prachtvollen goldgelben Säulen vom Zers. 146°C. aus. Ausbeute 70 Proc. d. Th. (1.7 gr.). Mit konz. Schwefelsäure färbt es sich blutrot→violetrot.

Anal.: Subst. = 4.778; AgBr = 6.603 mg. Subst. = 6.504 mg.; N_2 = 0.275 ccm., 15.5°C., 758 mm.
Gef.: Br = 58.81; N 4.90%. Ber. für $C_{19}H_{21}O_3N_3Br_6$ (819): Br = 58.55; N = 5.16%.

5. 1-Brom-dehydro-*l*-thebenon-7-keto-furazan (VI). 0.6 gr. des-N-Methyl-1-brom-sinomeninon-furazan (V) wird durch einstündiges Kochen mit Jodmethyl in 20 ccm. Methanol in das Jodmethylat übergeführt. Da das Jodmethylat nicht krystallisierend ist, wird der ölige Rückstand wieder mit 6 ccm. 16.5 Proc. Kalilauge halbstundenlang gelinde gekocht. Allmählig geht das Öl unter Trimethylamin-Abspaltung in Krystallmassen über. Nach dem Kühlen wird es von der Kalilauge abgetrennt, mit Wasser und Methanol gut nachgewaschen.

Durch zweimaliges Lösen in heissen Eisessig und Ausfällen mit Wasser wird das Produkt analysenrein, und schmiltzt bei 191°C.

Anal.: Subst. = 4.952; CO_2 = 9.903; H_2O = 1.916 mg.
Subst. = 4.372; AgBr = 2.240 mg. Subst. = 5.517 mg.; N_2 = 0.360 ccm., 18.5°C, 754 mm.
Gef.: C = 54.54; H = 4.30; Br = 21.80; N = 7.43%.
Ber. für $C_{17}H_{15}O_3N_2Br$ (375): C = 54.40; H = 4.03; Br = 21.31; N = 7.47%.

6. 9?-Brom-dehydro-*l*-thebenon-7-keto-furazan (XII). 1.0 gr. Dehydro-*l*-thebenon-7-keto-furazan (XI) wird in 40 ccm. Eisessig heiss gelöst und bei 15°C. mit 1 Mol. Brom (0.54 gr. Brom in 5.4 ccm. Eisessig) vorsichtig bromiert.

Nach 2 stündigem Stehenlassen bei der Zimmertemperatur wird es mit viel Wasser verdünnt. Der dabei amorph ausfallende Niederschlag wird gesammelt und durch Rühren mit Aceton in Krystallen übergeführt. Farblose Tafeln. Schmelzp. 152° ~ 153°C. Halochromie in konz. Schwefelsäure gelb→gelblich grün.

Anal.: Subst. = 5.185; CO_2 = 10.326; H_2O = 1.986 mg.
Subst. = 5.125; AgBr = 2.545 mg. Sust. = 4883 mg.; N_2 = 0.326 ccm. 19°C., 760 mm.
Gef.: C = 54.31; H = 4.26; Br = 21.13; N = 7.64%.
Ber. für $C_{17}H_{15}O_3N_2Br$ (375): C = 54.40; H = 4.03; Br = 21.31; N = 7.47%.

7. 1, 9?-Dibrom-dehydro-*l*-thebenon-7-keto-furazan (X). Diese Substanz wird in vier verschiedenen Wegen dargestellt.

a. Durch Bromierung von Dehydro-*l*-thebenon-7-keto-furazan (XI) mit 2 Mol. Brom. 1.0 gr. Substanz wird in 30 ccm. Eisessig heiss gelöst und bei der Zimmertemperatur dreistundenlang stehen gelassen. Man verdünnt dann mit wenig Wasser, wobei 1.0 gr. von (X) in schönen Prismen auskrystallisiert. Schmelzp. 210°~211°C.

b. Durch Bromierung von 9?-Brom-dehydro-*l*-thebenon-7-keto-furazan (XII) mit 1 Mol. Brom. 0.4 gr. Substanz wird in 10 ccm. Eisessig mit 0.17 gr. Brom (zehnfach verdünnt mit Eisessig) in üblicher Weise bromiert. Schon beim halbstundigen Stehenlassen bildet schöne Krystallen von (X). Ausbeute 0.4 gr.

c. Durch Bromierung von 1-Brom-dehydro-*l*-thebenon-7-keto-furazan (VI) mit 1 Mol. Brom. 0.9 gr. Substanz, gelöst in 30 ccm. Eisessig, wird mit 0.4 gr. Brom bei 15°C. vorsichtig bromiert. Nach zwei Stunden wird auf 100°C. zehn Minuten erhitzt. Beim Verdünnen mit wenig Wasser erhält man 1.0 gr. schön krystallisierte Substanz (X).

d. Durch Ether-Ringschluss von des-N-Methyl-1, 9? dibrom-sinomeninon-furazan (VIII). 0.3 gr. Substanz (VIII) wird durch einstundiges Kochen mit Methyljodid und Methanol ins Jodmethylat übergeführt. Das Jodmethylat ist aber nicht krystallisiered, deshalb hat man den ölige Rückstand direkt mit zehnfachen Menge von 16.5 Proc. Kalilauge abgebaut. Die Krystallen werden gesammelt, aus Eisessig und Wasser umkrystallisiert und identifiziert.

Anal.: Subst. = 5.490; CO_2 = 9.059; H_2O = 1.751 mg.
Subst. = 3.804; AgBr = 3.189 mg. Subst. = 5.841 mg.; N_2 = 0.318 ccm., 18.5°C., 757 mm.
Gef.: C = 45.02; H = 3.54; Br = 35.68; N = 6.21%.
Ber. für $C_{17}H_{14}O_3N_2Br_2$ (454): C = 44.93; H = 3.11; Br = 35.21; N = 6.17%.

Beim Kochen dieser Substanz mit Silberacetat in Eisessig oder methylalkoholischem Kali erhält man die unveränderte Substanz quantitativ zurück.

8. Dihydro-des-N-methyl-1-Brom-sinomeninon-furazan (XVI). 1.5 gr. Dihydro-des-N-methyl-sinomeninon-furazan werden in 15 ccm. Eisessig mit der berechneten Menge Brom (1 Mol., zehnfach verdünnt mit

Eisessig) bei 16°C. bromiert. Beim Abdestillieren von Eisessig krystallisiert das Hydrobromid schon aus. Es wird mit Aceton gewaschen und aus heissem Wasser umkrystallisiert. Lange Nadeln. Schmp. 259°C. (u. Z.). Ausbeute sehr gut.

Subst. = 3.822; AgBr = 2.813 mg. Gef.: Br = 31.06%.
Ber. für $C_{19}H_{25}O_3N_3Br_2$ (503): Br = 31.87%.

Die freie Base wird daraus mit Soda oder Ammoniak angefällt und aus Aceton umkrystallisiert. Prismen vom Zers. 221°~223°C. (sintern 207°C.).

Anal.: Subst. = 4.408; CO_2 = 8.759; H_2O = 2.258 mg.
Subst. = 3.606; AgBr = 1.664 mg. Subst. = 4.994 mg.; N_2 = 0.410 ccm., 16°C., 760 mm.
Gef.: C = 54.19; H = 5.69; Br = 19.64; N = 9.53%.
Ber. für $C_{19}H_{24}O_3N_3Br$ (422): C = 54.03; H = 5.69; Br = 18.96: N = 9.95%.

9. 1-Brom-*l*-thebenon-7-keto-furazan (XVIII). (*a*) *Durch Ringschluss.* 0.7 gr. Dihydro-des-N-Methyl-1-brom-sinomeninon-furazan-jodmethylat wird mit 9 ccm. 16.5 Proc. Kalilauge gelinde gekocht. Unter Entwickelung von Trimethyl-amin-geruch umwendelt sich das schwimmende Oel in Krystall in fünf Minuten. Nach halber Stunde werden die Krystalle gesammelt, in Eisessig gelöst und mit Wasser gefällt. Beim schwachen Erwärmen geht der flockige Niederschlag schnell in Krystallen. Ausbeute sehr gut. Schmp. 202°~203°C.

(*b*) *Durch Bromierung.* 0.7 gr. *l*-Thebenon-7-keto-furazan in 7 ccm. Eisessig gelöst, wird mit 0.37 gr. Br. (1 Mol.; in 3.7 ccm. Eisessig) bei Zimmertemperatur bromiert. Beim Stehenlassen krystallisiert das Produkt in Prismen aus. Ausbeute etwa 70 Proc. Schmp. 202°~203°C. (auch die Mischprobe).

Die Substanz ist schwerer löslich in Methanol, Alkohol und Eisessig als das nicht bromierte Substanz. Es gibt keine Halochoromie in Schwefelsäure.

Anal.: Subst. = 6.116; CO_2 = 12.173; H_2O = 2.476 mg.
Subst. = 5.518; AgBr = 2.755 mg. Subst. = 3.663 mg.; N_2 = 0.235 ccm., 13°C., 760 mm.
Gef.: C = 54.28; H = 4.50; Br = 21.25; N = 7.55%.
Ber. für $C_{17}H_{17}O_3N_2Br$ (377): C = 54.09; H = 4.51; Br = 21.22; N = 7.43%.

10. Perbromid von des-N-Methyl-1, 9?-dibrom-demethoxy-desoxo-dihydro-sinomenin (XIV). 0.4 gr. Substanz (XIII) wird mit 3 Mol. Brom in ganz analoger Weise wie bei der Darstellung von Furazan-Perbromid (IX) bromiert. Ausbeute 0.7 gr. Aus heissem Eisessig umkrystal-

lisiert, stellt die Substanz schöne goldgelbe Säulen dar. Zers. 112° ~113°C.

Halochromie in konz. Schwefelsäure blutrot→violetrot→dunkelbraun→schmutzig grün→violet.

Subst. = 4.116; AgBr = 5.507 mg. Subst. = 7.785 mg.; N_2 = 0.132 ccm., 19°C., 760 mm.
Gef.: Br = 56.94; N = 1.94%.
Ber. für $C_{19}H_{26}O_2NBr_5$ (700): Br = 57.06; N = 2.00%.

11. des-N-Methyl-1, 9?-dibrom-demethoxy-desoxo-dihydro-sinomenin (XV). 0.4 gr. Perbromid (XIV) wird mit 10 ccm. Aceton halbstundenlang auf 100°C. erhitzt und dann mit verdünntem Ammoniak ausgefällt. Ausbeute 0.2 gr. Aus heissem Methanol umkrystallisiert. Prachtvolle Säuren von Zers. 205°C.

Anal.: Subst. = 3.731; CO_2 = 6.858; H_2O = 1.817 mg.
Subst. = 3.573; AgBr = 2.909 mg. Subst. = 2.826 mg.; N_2 = 0.072 ccm., 15°C., 760 mm.
Gef.: C = 50.13; H = 5.41; Br = 31.68; N = 2.97%.
Ber. für $C_{19}H_{25}O_2NBr_2$ (459): C = 49.45; H = 5.45; Br = 34.86; N = 3.05%.

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AN EFFECT OF POTASSIUM CYANIDE ON THE OXIDATION-REDUCTION POTENTIAL.

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On the oxidation-reduction potential of the ferri-ferro complex cyanide solution many researches have been carried out and reported.

The first one who determined the potential was Fredenhagen[1] and in his experiment the ratio of ferricyanide to ferrocyanide was varied. Schaum and Linde,[2] using potassium ferricyanide and sodium ferrocyanide, obtained the following formula as the result of their experiment.

(1) *Z. anorg. Chem.*, **29** (1902), 396.
(2) *Z. Elektrochem.*, **9** (1903). 407.

$$E = E_0 + 0.0002T \log \frac{\text{(total Ferricyanide)}}{\text{(total Ferrocyanide)}}$$

In their experiment the total concentration of complex cyanide was constant, the ratio only being changed. The addition of some electrolytes displays a powerful influence on the potentials of oxidation-reduction. In acidic solution, potassium ferrocyanide acts as an oxidizing agent and therefore we can determine the concentration of the salt with hydrogen iodide. While in neutral potassium ferrocyanide plays a reducing action to convert iodine to iodide, as follows.

$$2Fe(CN)_6^{---} + 2I^- \rightleftarrows 2Fe(CN)_6^{----} + I_2$$

Schoch[1] measured the potential in the presence of 0.05 molal hydrochloric acid, varying the ratio of ferricyanide to ferrocyanide. Lewis and Sargent[2] showed that the presence of potassium ion added as potassium chloride had a large influence to lift the oxidation potential and explained this result that the added potassium ions decrease the concentration of ferrocyanide ions. Müller[3] found that the relation between the potential and the concentration of potassium ion using potassium hydroxide is as follows (at 0°C.).

$$E = E_0 + 0.0546 \log \frac{\text{(total ferricyanide)}(K^+)}{\text{(total ferrocyanide)}}$$

According to Schoch and Felsing[4] the relation is as follows;

$$E = E_0 + 0.0591 \log \frac{(Fe(CN)_6^{---})(K^+)^x}{(Fe(CN)_6^{----})}$$

and the value of x varies between 0.725 and 0.75. They obtained these relation using potassium chloride at 25°C. Linhart[5] also investigated the influence of potassium chloride in the similar manner.

Moreover, on the influence of hydrogen ion, Müller and Kolthoff[6] reported their results. The former obtained the following equation at 18°C.,

$$E = E_0 - 0.546 \log (H^+)^2$$

(1) *J. Am. Chem. Soc.*, **26** (1904), 1422.
(2) *J. Am. Chem. Soc.*, **31** (1909), 355.
(3) *Z. physik. Chem.*, **88** (1914), 46.
(4) *J. Am. Chem. Soc.*, **38** (1916), 1928.
(5) *J. Am. Chem. Soc.*, **39** (1917), 615.
(6) *Z. anorg. Chem.*, **110** (1920), 143.

while the latter at the same temperature,

$$E = 0.416 - 0.0577 \log (H^+)^{2.22}$$

and in the experiments the ratio of ferricyanide to ferrocyanide was 1:1, each concentration being ½(0.025) mol per litre. In this investigation the influence of added potassium cyanide was measured at the various concentration of the salt.

Experimental Part.

The apparatus used is shown in the diagram. A: Hydrogen inlet; B: Thermometer; C: Platinum electrode; D: Solution inlet; E: Hydrogen outlet; F: Salt bridge (0.1 m KCl); G: Salt vessel (0.1 m KCl); H:

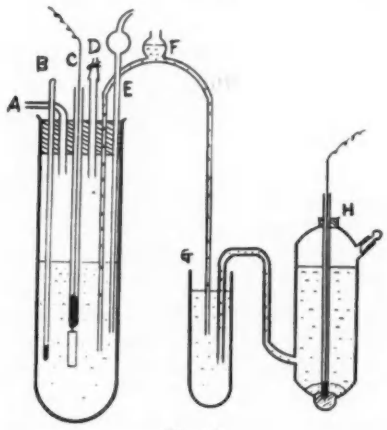


Fig. 1.

Calomel electrode. This investigation was carried out in the hydrogen atmosphere. Because in the alkaline solution, as we described above, potassium ferrocyanide behaves as a pretty powerful reducing agent in contact with air as following.

$$2Fe(CN)_6^{----} + \frac{1}{2}O_2 + HO \rightleftarrows 2Fe(CN)_6^{---} + 2OH^-$$

Potassium ferricyanide and ferrocyanide employed were of Kahlbaum's, and each was made into 0.05 molal solution with distilled water at the least contact of air. The potassium cyanide was also of high

purity and standardised with 0.1 normal silver nitrate solution. Potassium cyanide was added in the mixture of each 10 c.c. of the ferricyanide and ferrocyanide solution and the volume of this solution was enlarged to 50 c.c. with distilled water. Thus the ratio of ferricyanide to ferrocyanide was 1 : 1, and each of these concentration was 0.01 molal. The vessel was filled with hydrogen before the solution was poured into it. The hydrogen gas was prepared by using pure metallic zinc and sulphuric acid, and washed with potassium permanganate and then potassium hydroxide.

The electrode used was non-platinized platinum plate of about 1 cm.$\times$3 cm. The construction of the cell was as follows;

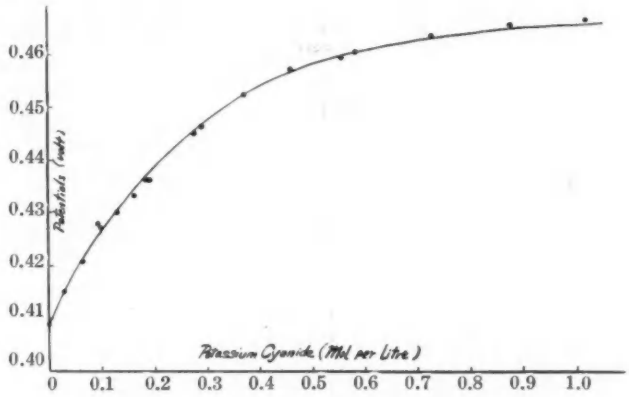
$$Pt\,|\,K_4Fe(CN)_6,\ K_3Fe(CN)_6,\ KCN\,|\,0.1\,mKCl\,|\,0.1\,mKCl,\ Hg_2Cl_2\,|\,Hg$$

The temperature of the cell was kept constant at 30°$\pm$0.05°C. in a thermostat. The results are shown in the table.

$K_4Fe(CN)_6$	$K_3Fe(CN)_6$	KCN	E_c	E_h*	E_h (calc.)
0.01	0.01	0	0.0684	0.4094	
0.01	0.01	0.0321	0.0747	0.4157	0.4130
0.01	0.01	0.0642	0.0798	0.4208	0.4238
0.01	0.01	0.0963	0.0855	0.4265	0.4300
0.01	0.01	0.1284	0.0892	0.4302	0.4344
0.01	0.01	0.1605	0.0920	0.4330	0.4379
0.01	0.01	0.1926	0.0953	0.4363	0.4409
0.01	0.01	0.0922	0.0872	0.4282	0.4294
0.01	0.01	0.1844	0.0950	0.4360	0.4400
0.01	0.01	0.2766	0.1040	0.4450	0.4468
0.01	0.01	0.3688	0.1113	0.4523	0.4507
0.01	0.01	0.4610	0.1165	0.4575	0.4541
0.01	0.01	0.5532	0.1182	0.4592	0.4569
0.01	0.01	0.2895	0.1052	0.4461	0.4469
0.01	0.01	0.5730	0.1194	0.4604	0.4576
0.01	0.01	0.7238	0.1220	0.4630	0.4610
0.01	0.01	0.8685	0.1242	0.4652	0.4633
0.01	0.01	1.0132	0.1252	0.4662	0.4662
0.01	0.01	1.1580	0.1257	0.4667	0.4663

* Potential of 0.1 normal KCl-calomel electrode : $0.3387+7.9\times10^{-4}(t-25)$.
Kust Arudt, Physikalische-chemie Tecknik, (1923) 795.
Auerbach, *Z. Elektrochem.*, **18** (1912), 13.
Lewis and Brighton, Sebastian. *J. Am. Chem. Soc.*, **39** (1917), 2245.
Fales and Vasbargh, ibid., **40** (1918), 291.

In the table E_c is the measured potential against a decinormal calomel electrode and E_h is the potential against a hydrogen electrode at 25°C. and Fig. 2 shows the value of E_h by the changes of concentrations of potassium cyanide.



From the data, we obtained the following approximate formula

$$E = 0.4660 + 0.0601 \log K^{0.59}$$

where K is the concentration of the potassium cyanide added. The last column in the above table shows the calculated values by this equation.

Under sunlight, we practised many investigations, but all those were worthless giving no systematic results. This is probably due to the decomposition of double cyanide by sun beams. So the author carried out this investigation in the dark room. The effect of more concentrated cyanide is more or less uncertain giving the fluctuation of potential by some disturbance.

Summary.

(1) The effect of the existence of potassium cyanide upon the oxidation-reduction potential of potassium ferricyanide and ferrocyanide was investigated.

(2) The investigation was performed in the hydrogen atmosphere in the dark room to avoid the atmospheric oxidation and the photochemical decomposition.

(3) The result can be expressed approximately by the following empirical formula at 30°C.

$$E = 0.4660 + 0.0601 \log K^{0.59}$$

where K is the concentration of potassium cyanide, and each concentration of potassium ferricyanide and potassium ferrocyanide is 0.01 mol. respectively.

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THE ACTIVITY COEFFICIENT OF ZINC SULPHATE FROM ELECTROMOTIVE FORCE MEASUREMENTS.

By Kosaku MASAKI and Takuo IKKATAI.

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In the early days of the development of the activity coefficient few investigators[1] reported on the activity coefficient of zinc sulphate in the following cell

$$\mathrm{Zn\,(amalgam)\,|\,ZnSO_4(m),\ Hg_2SO_4(s)\,|\,Hg} \quad \ldots\ldots\ldots\ldots \quad (1)$$

but the results may be uncertain by the solubility of mercurous sulphate. Recently Cowperthwaite and LaMer[2] had the excellent investigation upon the cell

$$\mathrm{Zn\,(2\ phase\ amalgam)\,|\,ZnSO_4(m),\ PbSO_4(s)\,|\,Pb(2\ phase\ amalgam)} \ldots \quad (2)$$

and determined the activity coefficient of zinc sulphate in the various concentrations which is in good conformity with the predictions of the Gronwall, LaMer and Sandved's[3] extension of the Debye-Hückel theory.[4]

In this investigation we measured the electromotive force of the cell (1) with a more concentrated range on which Cowperthwaite and LaMer made no investigation and we calculated the activity coefficient of zinc sulphate.

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(1) Lehfeldt, *Z. physik. Chem.*, **35** (1900), 257; Cohen, Chattaway and Tombrock, *Z. physik. Chem.*, **60** (1907), 706; **61** (1907), 384; **75** (1910), 1.

(2) *J. Am. Chem. Soc.*, **53** (1931), 4333.

(3) *Physik. Z.*, **29** (1928), 358.

(4) Ibid, **24** (1923), 185.

Theoretical.

Debye and Hückel introduced an approximate equation early in the development of their theory of strong electrolytes, solving the Poisson's equation by retaining only the linear term resulting from the expansion of the exponential in the Boltzmann's expression for the density of electricity for mathematical simplicity and they had many experimental investigations which demonstrated that the activity coefficients of strong electrolytes in aqueous solution agree fairly well with the predictions given by their equations. But even in regions of high dilution there are serious discrepancies between the calculated values from these equations and the experimental data. Gronwall, LaMer and Sandved obtained the following expression, solving the Poisson's equation by using the complete form of the Boltzmann's expression, for the activity coefficient of an electrolyte of symmetrical type, i.e. $Z_1 = -Z_2 = Z$.

$$\log f = -\frac{\epsilon^2 Z^2}{kTDa} \times \frac{1}{2} \times \frac{x}{1+x} + \sum_{m=1}^{\infty} \left(\frac{\epsilon^2 Z^2}{kTDa}\right)^{2m+1} \left[\frac{1}{2} X_{2m+1}(x) - 2m Y_{2m+1}(x)\right]. \quad (3)$$

In the above equation, $x = Ka$, and $K = \sqrt{\frac{8\pi N \epsilon^2 Z^2 c}{1000 kTD}}$, D is the dielectric constant of water ($D = 78{,}54[1 - 0.0046(t-25) + 0.0000088(t\text{-}25)^2]$)[1], Z is the valence of the cation and anion, ϵ is the charge of an electron ($\epsilon = 4.774 \times 10^{-10}$), k is Boltzmann's constant ($k = 1.372 \times 10^{-16}$), N is Avogadro's number ($N = 6.061 \times 10^{23}$), $\bar{a}$ is the distance of closest approach of the two ions, c is the concentration in moles per litre of solution, and $X(x)$ and $Y(x)$ are known functions of x.

Putting numerical values in (3) Gronwall, LaMer and Sandved got the following working equation

$$-\log_{10} f = 1.53636\left(\frac{Z^2}{a}\right)\frac{x}{1+x} - 0.15382\left(\frac{Z^2}{a}\right)^3 \cdot 10^3\left[\frac{1}{2}X_3(x) - 2Y_3(x)\right]$$
$$-0.0770\left(\frac{Z^2}{a}\right)^5 \cdot 10^5\left[\frac{1}{2}X_5(x) - 4Y_5(x)\right] \quad \ldots\ldots\ldots\ldots \quad (4)$$

Numerical values for the functions $10^3[\frac{1}{2}X_3(x) - 2Y_3(x)]$ and $10^5[\frac{1}{2}X_5(x) - 4Y_5(x)]$ were tabulated by the Gronwall, LeMer and Sandved for various assigned values of x. Therefore the value for these functions at any desired x may be obtained from their tables by interpolation.

Wyman, *Phys. Rev.*, **35** (1930), 623.

The electromotive force of the cell (1), corresponding to the following process.

$$Zn(solid)+Hg_2SO_4(solid) = Hg(liquid)+ZnSO_4(m) \quad \cdots\cdots\cdots (5),$$

is given by the equation

$$\begin{aligned} E &= E_0-\frac{RT}{2F}\ln m_{Zn^{++}}\cdot f_{Zn^{++}}-\frac{RT}{2F}\ln m_{SO_4^{--}}\cdot f_{SO_4^{--}} \\ &= E_0-\frac{RT}{2F}\ln m_{Zn^{++}}-\frac{RT}{2F}\ln m_{SO_4^{--}}-\frac{RT}{2F}\ln f_{Zn^{++}}\cdot f_{SO_4^{--}} \\ &= E_0-\frac{RT}{2F}\ln m_{Zn^{++}}-\frac{RT}{2F}\ln m_{SO_4^{--}}-\frac{RT}{F}\ln f\pm \quad \cdots\cdots\cdots (6) \end{aligned}$$

For 25°C., this equation (6) takes the following form

$$E = E_0-0.05915\log m-0.05915\log f \quad \cdots\cdots\cdots (7)$$

For convenience in plotting and calculating the mean activity coefficient $f_{ZnSO_4}=\sqrt{f_{Zn^{++}}\cdot f_{SO_4^{--}}}$, we calculate the quantity E_0', where

$$E_0' = E+0.02957\log m+0.02957\log m \quad \cdots\cdots\cdots (8)$$

$$E_0' = E_0-0.05915\log f \quad \cdots\cdots\cdots (9)$$

and the intercept of extrapolated E_0' at zero concentration gives the value of E_0.

Experimental.

Preparation of Materials. Mercurous sulphate: Kahlbaum's "for analysis" was employed and kept in the dark room.

Zinc sulphate: Kahlbaum's "for analysis" was employed without recrystallization. The salt was dissolved in conductivity water and stored in a steamed-out hard glass flask equipped with a stopper which was deviced to make the evaporation least possible.

Mercury: Purified mercury was washed ten times with a mixture of dilute mercurous nitrate and nitric acid and distilled thrice in a reduced pressure with a current of air.

Zinc: A. purest profitable zinc stick was employed.

Zinc amalgam: The zinc stick stated above was attached to a nip of a Pt wire which was sealed into a glass tube at the end. Then the joint and Pt part was covered with highest grade sealing wax, and the zinc was amalgamated after being scraped clean from oxide.

Analysis of Zinc Sulphate Solution. Kahlbaum's zinc sulphate was dissolved in conductivity water to form a stock solution from which dilutions were made by weight. Besides, a weighed salt was dissolved in a weighed quantity of conductivity water to prove the accuracy of the analytical method employed. The determinations of the concentration was performed as described by Cowperthwaite and LaMer. A weighed sample of the solution was carefully evaporated to dryness in a steam oven and then the residue was heated in an air oven at 300°C. for several hours after treated with a small quantity of strong sulphuric acid. Then the bottle was cooled in a desiccator and weighed. Then treating with sulphuric acid, heating at 300°C. and weighing were repeated till the weight of the dried mass became constant. The residue was the weight of anhydrous zinc sulphate. This method is quite satisfactory. The reference solution which was made to be 1.03955 mol was determined by this method as 1.03967 mol. The error was only 0.02% and in a region of the experimental error. The stock solution was determined as 1.16994 mol.

Experimental Method. According to Landolt's "Physikalisch-chemische Tabellen" the system of zinc-mercury forms no compound nor solid solution and the composition of the liquid phase is definite at a given temperature when the solid phase coexists. Hence an amalgamated zinc can be employed as a reversible and reproducible zinc electrode. We made pairs of electrodes mentioned above and each of them was proved to be identical within 0.02 mv. They were kept in the nitrogen atmosphere to prevent the oxidation. But in its practical employment at the temperature 25°C. the presence of air is considered to give a little effect on it. The cells gave a constant electromotive force within two or six hours even in air. A slight scum on the surface of the cathode was found after four days.

The zinc sulphate solutions which were made by weight from the stock solution were saturated with mercurous sulphate in a thermostat maintained at 25°+0.05°C. for two days with frequent shaking. The cells used had the special form as Fig. 1. In this figure, 1: the red wax, 2: zinc amalgam. The electromotive forces of the cell were measured after being kept in the thermostat at

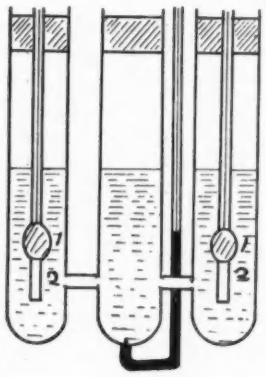

Fig. 1.

25°C. for one hour and the average values of two or three cells were described in the table.

Experimental Data. The experimental values of the electromotive force and the computed function E are given in Table 1. The observed electromotive force given in column 3 is the average value of two or three cells, each of the cell being nearly idential with a little difference of 0.05 mv. A correction for the solubility of mercurous sulphate is

Table 1.

E.M.F. of the Cell Zn-Hg(sat. amalgam) | $ZnSO_4(m)$, $Hg_2SO_4(s)$ | Hg at 25°C.

No.	Molality of $ZnSO_4$	E (obs.)	Molality of total SO_4^{--}	0.02957 log m Zn^{++}	0.02957 log m SO_4^{--}	E_0'
1	3.000	1.43048	3.000	+0.01411	+0.01411	1.45870
2	2.500	1.43646	2.500	.01177	.01177	1.46000
3	2.000	1.44375	2.000	.00891	.00891	1.46156
4	1.800	1.44648	1.800	.00755	.00755	1.46158
5	1.600	1.44803	1.600	.00604	.00604	1.46010
6	1.400	1.45094	1.400	.00432	.00432	1.45958
7	1.000	1.45595	1.000	.00000	.00000	1.45595
8	1.16994	1.45415	1.17014	.00202	.00202	1.45819
9	0.934504	1.45736	0.934676	− .00087	− .00087	1.45562
10	.699756	1.46240	.699959	.00458	.00458	1.45108
11	.465742	1.46547	.465939	.00981	.00981	1.44585
12	.387925	1.46708	.388101	.01216	.01216	1.44276
13	.232547	1.47292	.232736	.01874	.01873	1.43535
14	.165698	1.47736	.165909	.02309	.02308	1.43119
15	.128833	1.48073	.129053	.02632	.02630	1.42811
16	.105386	1.48301	.105639	.02890	.02887	1.42524
17	.0891541	1.48498	.0893737	.03104	.03101	1.42293
18	.0772633	1.48663	.0774078	.03288	.03285	1.42090
19	.0681679	1.48832	.0684336	.03449	.03444	1.41939
20	.0609883	1.48973	.0612565	.03592	.03586	1.41795
21	.0441321	1.49295	.0444176	.04008	.04001	1.41286
22	.0101087	1.51370	.0105397	0.5901	.05847	1.39622
23	.0039726	1.52326	.0045819	.07101	.06916	1.38303
24	.0020793	1.52808	.0028429	.07932	.07529	1.37347
25	.0008558	1.53310	.0018150	.09072	.08106	1.36132
26	.0004321	1.53465	.0015055	.09950	.08346	1.35169

necessary at the concentration of 0.232547 molal solution or less. This was made by calculating the increase of concentration of sulphate ion in the solution which is due to the slight solubility of the mercurous sulphate, and calculating the potential resulting therefrom.

Drucker[1] reported the solubility of mercurous sulphate at 25°C. to be 11.71×10^{-4} mol per litre. LaMer and Parks[2] studied the parameter of $CdSO_4$ and reached to the conclusion that the value is larger than 3.6 Å but less than 3.7 Å. Also Cowperthwaite and LaMer got the value 3.64 Å for zinc sulphate. Hereupon we assumed that for mercurous sulphate the parameter $\bar{a}$ is 3.7 Å. Then by the Gronwall, LaMer and Sandved's equation we can find the activity coefficient f as 0.704. In order to calculate the increase in sulphate ion we used the equation

$$m_{Hg_2^{++}} \cdot f_{\pm} \cdot m_{SO_4^{--}} \cdot f_{\pm} = a_{Hg_2^{++}} \cdot a_{SO_4^{--}} = k = 6.80\times10^{-7}$$

Then an approximation was performed as

$$x(fm+x) = k \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where x is the mean activity resulting from the mercurous sulphate dissolved, and the mean activity coefficient was calculated by (4) at concentration m. The solubility was obtained by x/f. Accurately saying, f is the mean activity coefficient at $m+f/x$, and repeated calculations are necessary for dilute solutions. The procedure is as follows.

The solubility m_1 obtained by the first calculation was added to m and f_2 was calculated at $(m+m_1)$ and x_2 was obtained by (10). This procedure was repeated to get a practically constant solubility. For instance for No. 26.

By 1st calculation	2nd	3rd	4th	5th	6th
$m_{Hg_2SO_4} = 0.000842$	0.0010276	0.0010659	0.0010720	0.0010734	0.0010734

The values of E_0' are shown graphically in Fig. 2. The values for dilute solutions, where the solubility of mercurous sulphate amounts to some 4% or more of the total concentration, abnormally decreases with increasing dilution.

(1) *Z. anorg. Chem.*, **28** (1901), 362.
(2) *J. Am. Chem. Soc.*, **53** (1931), 2040.

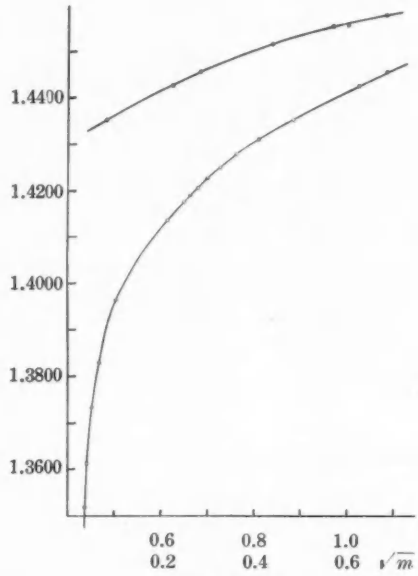

Fig. 2.

Discussion of Results. The abnormal decrease of E_0' in highly dilute solutions prevents us from the interesting application of the Gronwall, LaMer and Sandved's extension of the Debye-Hückel's theory. Because the extension is expected to be valid in the concentration range up to 0.01 molal solution. The cause of the anomaly can be attributed to either the self discharge effect or the absurd assumption that the parameter $\bar{a}$ of mercurous sulphate is 3.7 Å. Upon these problems we will render the same discussion in a following paper. Cowperthwaite and LaMer determined the activity coefficient of zinc sulphate in dilute solution at 25°C. as follows.

Molality	0.0005	0.001	0.002	0.005	0.01	0.02	0.05
Calc.	0.780	0.701	0.608	0.478	0.386		
Obs.	0.780	0.700	0.608	0.477	0.387	0.297	0.206

We used these data for the determination of E_0 and the activity coefficient in more concentrated parts. For by the equation

$$E_0' = E_0 - 0.05915 \log f$$

we can polt $E_0'-E_0$ against the square root of the molality to which the activity coefficient is assigned, and the extrapolation of our data to

higher dilutions was carried out strictly parallel to the curve $E_0'—E_0$. This is shown in Fig. 3.

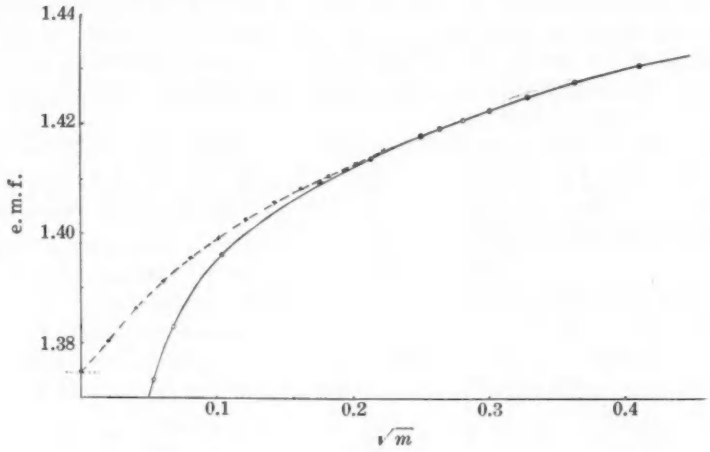

Fig. 3.

Table 2.

The Activity Coefficient of Zinc Sulphate at 25°C.

No.	Molality of total SO_4^{--}	Activity Coef. $E_0'=1.37375$	$E_0=1.37470$	$E_0=1.37480$
1	3.000	0.0381		
2	2.500	0.0362		
3	2.000	0.0341		
4	1.800	0.0340		
5	1.600	0.0361		
6	1.400	0.0368		
7	1.000	0.0422		
8	1.17014	0.0389	0.0388	0.0389
9	0.934676	0.0429	0.0429	0.0430
10	0.699959	0.0493	0.0492	0.0494
11	0.465939	0.0628	0.0627	0.0629
12	0.388101	0.0708	0.0707	0.0710
13	0.232736	0.0945	0.0943	0.0947
14	0.165909	0.1111	0.1107	0.1113
15	0.129053	0.1253	0.1251	0.1255
16	0.105639	0.1401	0.1400	0.1403
17	0.0893737	0.1533	0.1530	0.1536
18	0.0774078	0.1659	0.1656	0.1662
19	0.0684336	0.1759	0.1756	0.1762
20	0.0612565	0.1860	0.1856	0.1864

We find graphically joint of the E_0'—E_0 curve and the experimental E_0' curve where the dissolved mercurous sulphate is so little as to give no effect on the study of E_0. Thus we find E_0 as 1.37475. The activity coefficient calculated by this value for E_0 is tabulated in Table 2. The most possible value for E_0 is 1.37475, but two slightly different values are used to the calculation of the activity coefficient. These results are given in columns 2 and 3.

Using the values measured by Cowperthwaite and LaMer, we tabulated the activity coefficient of zinc sulphate for round concentration in Table 3. The third column was compiled from the data of LaMer and Parks for cadmium sulphate at 25°C.

Table 3.

Mean Activity Coefficient for Round Concentration.

Molality	$ZnSO_4$	$CdSO_4$
1.000	0.0422	0.0418
0.500	0.0596	0.0605
0.200	0.101	—
0.100	0.144	0.137
0.050	—	0.199
0.010	0.387	0.383
0.005	0.477	0.476
0.002	0.608	—
0.001	0.700	0.699
0.0005	0.780	0.774

Summary.

1. Electromotive forces of the cell, Zn-Hg (sat amalgam) | $ZnSO_4(m)$, $Hg_2SO_4(s)$ | Hg, were measured at 25°C. in the range of the concentrations of 0.0004321 to 3 molal.

2. The electromotive force of higher dilutions is quite abnormal owing to the solubility of mercurous sulphate.

3. The mean activity coefficients of zinc sulphate for more concentrated parts were calculated by using the Cowperthwaite and LaMer's data about dilute solutions. The potential E_0 of the cell, when ion activities of zinc sulphate are hypothetically one molal, was found to be 1.37475 volt at 25°C.

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STUDIES ON REACTIONS BETWEEN GAS AND SOLID. IV. AZOTATION OF CALCIUM CARBIDE AND THE EFFECT OF TEMPERATURE ON ITS VELOCITY.[1]

By Takeo AONO.

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Experimental.

Experimental Procedure. The method and apparatus of these experiments were nearly the same as those reported in the former paper.[2] But in this case the pressure of nitrogen was kept constant (1 atm.) and the velocity of the reaction was determined by measuring the speed of absorption from time to time with a second differential manometer of bromonaphthalene attached to the reaction tube. At the end of the reaction or after a difinite time the tube was rapidly cooled and the product was weighed and analysed. The content of nitrogen at a given moment was obtained by graphically integrating the $\left(-\frac{dP}{dt}\right.$ or $\left.-\frac{dm}{dt}\sim t\right)$ curve and comparing the integrated value with the final analysis.

Effect of Temperature. The effect of temperature on the reaction velocity is shown in Table 1 and Figs. 1, 2 and 3. The time was measured from the beginning of introducing nitrogen into the tube, and it took about ½–1 minute to reach 1 atm. From Fig. 1 we see that the velocity of absorption of nitrogen is very small at first and increases rapidly up to a maximum value and then gradually decreases. The results are similar to those obtained by H. H. Frank and his co-workers.[3]

The initial increase of the velocity is probably due to the following causes:

(a) liberation of the heat of reaction: $CaC_2+N_2=CaCN_2+C+54.8Cal.$,[4] which elevates the temperature of the reacting mass locally,[5] the greater the reaction velocity the greater will be the temperature elevation and consequent acceleration;

(1) Read before the Chemical Society of Japan, Dec. 1931.

(2) T. Aono, This Bulletin, **7** (1932), 143–154.

(3) H. H. Franck, F. Hochwald and G. Hoffmann, *Z. phys. Chem.*, Bodenstein-Festband, (1931), 985.

(4) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **34** (1931), 890.

(5) The local elevation of temperature was measured and reported by G. Bredig, *Z Elektrochem.*, **13** (1907), 69.

Table 1.

Azotation velocity of powdered carbide ($CaC_2 = 68.2$, $CaF = 1.2\%$) at various temperatures.

Temp. °C.	867		950		1000		1060		1090		1140	
Carbide, gr.	4.0043		4.0066		4.0055		4.0068		4.0002		4.0013	
Exp. No.	361		359		362		360		363		365	
Time, min.	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %	vel.	fix. %
1			1.100	1.16		0.76	0.356	0.23	0.441	0.43		
2	0.256	0.40	1.116	2.44	1.242	1.93	0.664	0.75	0.619	1.00	0.346	0.40
3	.265	0.65	1.077	3.62	1.443	3.41	1.44	1.79	1.001	1.86	1.266	1.26
4	.264	0.90	1.052	4.73	1.577	5.05	2.91	4.02	2.74	3.72	3.925	4.31
5	.253	1.14	1.016	5.82	1.625	6.80	4.085	7.81	7.25	8.91	9.10	11.80
6	.231	1.37	0.983	6.87	1.613	8.55	4.63	12.56	14.93	21.43	14.29	26.15
7			0.956	7.89			4.33	17.44	14.28	27.36	13.34	44.10
8	.198	1.77	0.922	8.87	1.528	12.00	3.51	21.58	9.01	40.43	8.13	56.90
9			0.890	9.83			2.86	24.80	5.88	59.80	5.99	65.35
10	.179	2.13	0.861	10.76	1.404	15.13	2.40	27.68	4.48	70.15	4.406	71.65
12	.161	2.45	0.807	12.51	1.250	17.98	1.85	32.05	2.52	77.95	2.355	79.60
14	.148	2.75	0.749	14.19	1.146	20.58	1.585	35.66	1.34	82.10	0.833	83.20
16	.139	3.04	0.728	15.72	1.026	22.95	1.415	38.84	0.588	84.10	0.350	84.50
18	.132	3.29	0.662	17.14	0.940	25.10	1.306	41.70	0.298	85.00	0.235	85.20
20	.125	3.53	0.615	18.46	0.869	27.05	1.241	44.40	0.211	85.60	0.172	85.70
25	.111	4.11	0.518	21.39	0.738	31.37	1.104	50.57	0.127	86.45	0.093	
30	.104	4.63	0.426	23.89	0.629	35.06	0.980	56.35	0.085	87.00	0.058	86.85
35	.092	5.13	0.379	26.00	0.554	38.28	0.836	61.20	0.061	87.45	0.037	
40	.085	5.58	0.341	27.90	0.505	41.08	0.718	65.30	0.045	87.75	0.027	87.40
45	.079	5.96	0.315	29.60			0.625	68.85	0.032	87.95	0.020	
50	.074	6.34	0.291	31.17	0.438	46.16	0.539	71.90	0.020	88.05		87.60
60	.066	7.01	0.251	34.02	0.391	50.65	0.407	77.10		88.15	0.000	87.80
70	.060	7.61	0.220	36.60	0.350	54.65	0.278	80.65				
80	.055	8 16	0.197	38.82	0.314	58.25	0.197	83.15				
90	.051	8.67	0.177	40.80	0.277	61.45	0.139	84.95				
100	.048	9.14	0.157	42.55	0.247	64.25	0.086	86.20				
120	.044	10.01			0.199	69.10						
140	.040	10.81			0.165	73.00						
160	.036	11.53			0.139	76.30						
180	.044	12.21			0.119	79.15						
200	.041	13.00			0.101	81.50						
220	.037	13.74			0.079	83.45						
240	.033	14.41			0.058	84.85						
260	.030	15.03										

(b) liberation of nascent carbon, which, according to the author's opinion, acts as an efficient catalyser for this reaction;

(c) action of the boundary between the new phase of minute crystal of $CaCN_2$ formed and the reacting CaC_2.

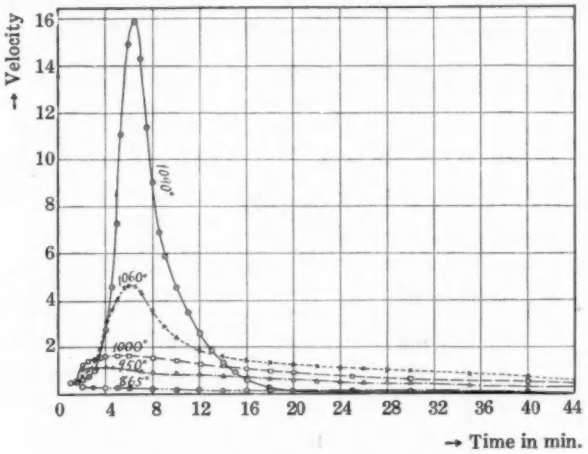

Fig. 1.—Reaction velocity and temperature.

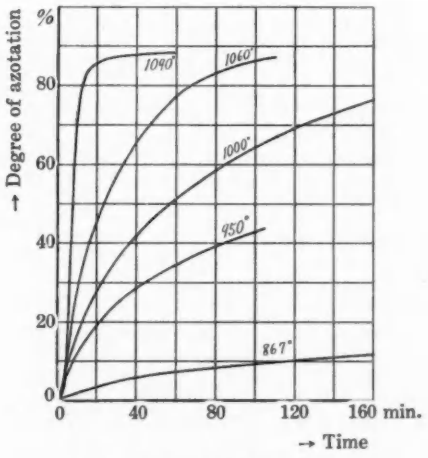

Fig. 2.—Degrees of azotation and temperature.

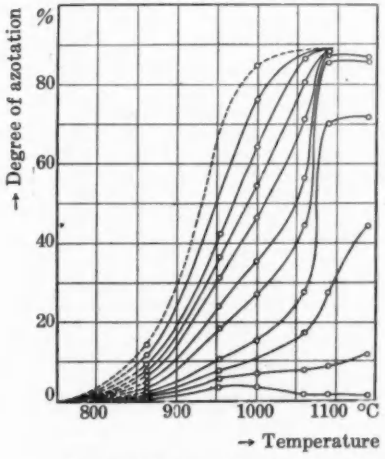

Fig. 3.—Degrees of azotation after definite times at various temperatures.

The time of the maximum velocity increases with rising temperature, and the degree of azotation (Y) at that time also increases with temperature as shown by the following equation.

$$\log Y = A - \frac{B}{T} ,$$

where A and B are constants and T the absolute temperature. (See Table 2 and Fig. 4).

Table 2.

Exp. No.	361	359	362	360	363	365
$1/T\times10^4$	8.78	8.18	7.86	7.50	7.34	7.08
Y	0.65	2.44	6.80	12.56	21.43	36.0
log Y	−0.19	0.39	0.83	1.10	1.31	1.55

The simple relation for the first order of the reaction velocity does not hold generally in this case, and the following integrated form does not give a constant value of k_4.

$$k_4 = \frac{1}{t-t_o} \ln \left(\frac{n_\infty - n_o}{n_\infty - n_t} \right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4_1)$$

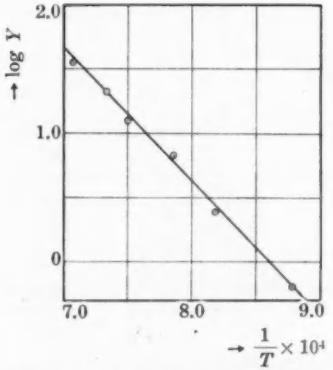

Fig. 4.—Relations btw. degrees of azotation (Y) before the time of velocity maximum and temperature.

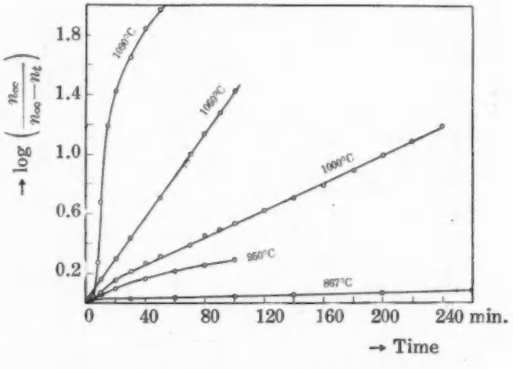

Fig. 5.—Relation btw. $\log \left(\frac{n_\infty}{n_\infty - n_t} \right)$ and time at various temps. (Powdered carbide).

where n_0 and n_t (%) are degrees of azotation at time t_0 and t (minutes) respectively, n_∞ the final maximum value of n_t, and k_4 a velocity constant.

As is shown in Fig. 5 and Table 3, the results at 1000° and 1060°C. satisfy the following relation after a certain time from the beginning,

$$k_4' = \frac{2.303}{t+t'} \log\left(\frac{n_\infty}{n_\infty - n_t}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (4_2)$$

in which k_4' and t' being constant. We have then

$$n_t = n_\infty\left(1 - e^{-k_4'(t+t')}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Table 3. Powdered carbide.

Relation btw. $\log_{10}\left(\frac{n_\infty}{n_\infty - n_t}\right)$ and time at various temperatures.

Exp. No.	361	359	362	360	363
Temp. °C	867	950	1000	1060	1090
t, min. 5					0.0457
10		0.0558	0.068	0.160	0.6741
20		0.1007	0.153	0.297	1.4178
30	0.0233		0.212	0.430	1.6484
40		0.1661	0.261		1.8525
50			0.308	0.704	1.9717
60	0.0354	0.2095			
70			0.388	1.000	
80		0.2489	0.446	1.132	
90			0.490	1.284	
100	0.0469	0.2824	0.534	1.421	
120			0.620		
140	0.0561		0.708		
160			0.797		
180			0.891		
200	0.0686		0.989		
220			1.085		
220			1.183		
260	0.0806				

Applying this relation to the data obtained from Exp. 360 at 1060°C., for example, we have $k_4' = 0.0320$, $t' = 1.5$ and therefore

$$n_t = 89.6\,\{1-e^{-0.0320(t+1.5)}\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4_4)$$

The values calculated by the equation (4_4) fairly well agree with the observed ones as shown in Table 4.

Table 4.

t	k_4'	n_t (obs.)	n_t (calc.)
10	0.0321	27.68	27.6
20	0.0318	44.40	44.5
30	0.0315	56.35	57.8
50	0.0315	71.90	72.5
70	0.0322	80.65	80.5
80	0.0323	83.15	83.0
90	0.0323	84.95	84.8
100	0.0322	86.20	86.2
110	0.0318	87.00	87.1
	Mean 0.0320		

At temperatures lower and higher than 1000–1060°C., the above relation is not fulfilled. At 950° and 867°C. the following relation, which was derived from the assumption that the layer of products retards the reaction,(1) was found to be satisfied:

$$\frac{\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2}{t-t'} = k_5' \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4_5)$$

where t' and k_5' being constant (Table 5). If we draw curves of $\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2$ against time, we have straight lines in the cases of Exp. 359 (950°C.) and 361 (867°C.). (Fig. 6).

Of course the relation 4_5 is not fulfilled at temperatures above 1000°C., and even at 867°C. it does not hold, if the carbide is mixed with catalysers such as active carbon (Exp. 521 at 867°C.) and calcium chloride (Exp. 523 at 867°C.), which are effective to accelerate the reaction. (See Table 5, Exp. No. 521; the numerical value of n_t will be found in the next paper).

(1) Vid. the next paper.

Table 5. Powdered carbide.

Relation between $\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2$ and time at 867° and 950°C.

Exp. No.	361		359		362	363	(521)
Temp. °C.	867		950		1000	1090	(867)
Time. min.	$\{\ \}^2$	$k_5'\times10^4$	$\{\ \}^2$	$k_5'\times10^4$	$\{\ \}^2$	$\{\ \}^2$	$\{\ \}^2$
10			0.0576	92.9		3.35	0.0036
20			0.152	93.8	0.25	9.50	.0100
30	0.00639	2.74	0.250	95.4		11.6	.0196
40			0.336	92.8		13.8	.0306
50			0.429	92.9		16.0	.0420
60	0.0146	2.74	0.518	92.2	1.145		.0566
70			0.609	92.0			(at t=62)
80			0.706	92.7			
90			0.784	91.0	1.99		
100	0.0253	2.72	0.865	90.0			
120					2.92		
140	0.0361	2.71					
180					4.97		
200	0.0530	2.74					
240					7.21		
260	0.0703	2.77					
t'	6.7		3.8				
Mean k_5		2.737		92.57			

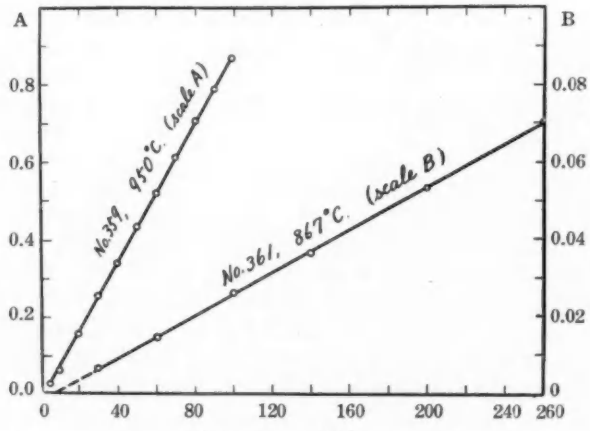

Fig. 6.—$\left\{n_\infty^{\frac{1}{3}}-(n_\infty-n_t)^{\frac{1}{3}}\right\}^2$ against time.

From the equation 4_5 we have

$$n_t = n_\infty - \left\{ n_\infty^{\frac{1}{3}} - \nu' k_5'(t-t') \right\}^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4_6)$$

The calculated values of n_t by this equation coinside fairly well with the observed ones. (Table 6).

Table 6. Exp. No. 361.

see errata V. 7, P. 407 ($n_\infty = 99.0$; $t' = 6.7$ min; $k_5' = 2.737 \times 10^{-4}$)

t. min.	30	60	100	140	200	260
n_t (obs.)	4.63	7.01	9.14	10.81	13.00	15.03
n_t (calc.)	4.68	7.00	9.21	10.93	13.05	14.82

The theoretical consideration of these relations will be given in the next paper.

Applying the Arrhenius' equation

$$\ln k = C - \frac{E}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4_7)$$

on the results obtained from Exps. No. 362 and 360, we have the apparent heat of activation E for the reaction

$$CaC_2 + N_2 = CaCN_2 + C$$

at the temperature between 1000 and 1060°C.:

$$E = 4.57 \log\left(k'_{T_1} / k'_{T_2} \right) \Big/ \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \ldots\ldots\ldots\ldots \quad (4_8)$$

see errata V. 7, P. 407

If we assume $N_\infty = 90.0$ in both cases, then we have $k_4 = 0.0309$ for 1060°C. and 0.0107 for 1000°C., and putting these values in the equation (4_8) we have $E = 58.6$ Cal./mol. for the temperatures between 1000 and 1060°C. Above the temperature of about 1080°C. the velocity increases suddenly and E becomes smaller (about 33 Cal./mol.). This may be due to the change in the phase of the reacting substance, e.g. partial fusion of the system CaC_2–$(CaCN_2)$–CaO–CaF_2.[1] At the same time the character of the velocity curve deviates from Equation 4_2, and

(1) H. H. Franck and H. Heimann, *Z. Elektrochem.*, **33** (1927), 469, reported that the lowest melting point of the system (CaC_2-CaF_2-CaO) is 1070°C.

also the reaction is too fast to be measured accurately at such higher temperatures.

These experiments were carried out in the research laboratory of the Denki-Kagaku-Kogyo Co., Ltd., Tokyo, before Sept. 10th, 1930, and reported to the meeting of directors and engineers of the company on that day. The author expresses his best thanks to Mr. K. Hibi, who gave him the opportunity of carrying out the experiments and allowed him to publish this report now, and to Mr. I. Kobayashi, who assisted him during the experiment.

Summary.

The effect of temperature elevation to the velocity of azotation of powdered calcium carbide (with 1% CaF_2) has experimentally been determined.

1. At a constant temperature lower than about 950°C., the following relation was found:

$$n_t = n_\infty - \left\{n_\infty^{\frac{1}{3}} - \sqrt{k_5'(t-t')}\right\}^3$$

where n_t means the degree of azotation (in %) after a time t, and n_∞ the final and maximum value of n_t; k_5 and t' are constants.

2. At a constant temperature between about 1000 and 1060°C., the common monomolecular course was found, namely:

$$n_t = n_\infty \left\{1 - e^{-k_4'(t+t')}\right\}$$

where k_4' being a velocity constant.

3. At any temperature there is a maximum in the velocity; the time and the degree of azotation at the maximum point increase with rising temperatures. The following approximate relation was found between them.

$$\log Y = A - \frac{B}{T},$$

where Y is the degree of azotation at the maximum of the velocity, T the absolute temperature, and A and B constants.

4. From the temperature coefficient of the velocity constant, the apparent heat of activation for a powdered technical carbide (with 1% CaF_2) was calculated to be about 58.6 Cal./mol. at temperatures between 1000° and 1060°C., and about 33 Cal./mol. above 1080°C.

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